

UNIT 11

REACTIONS OF AROMATIC COMPOUNDS-I

Structure

11.1 Introduction	Friedel-Crafts Acylation
Expected Learning Outcomes	Mechanism of Electrophilic Substitution
11.2 Reactions of Aromatic Compounds	11.4 Addition Reactions of Benzene
11.3 Electrophilic Aromatic Substitution Reactions	Addition of Halogen to Benzene
Nitration	Reduction
Halogenation	11.5 Summary
Sulphonation	11.6 Terminal Questions
Friedel-Crafts Alkylation	11.7 Answers

11.1 INTRODUCTION

In the previous Unit, we have discussed isolation, preparation of benzene and alkylbenzene. Benzene is the most important aromatic compound. In this unit we will study some important reactions of benzene.

Benzene is carcinogenic and injurious to health. Prolonged exposure to benzene leads to bone-marrow depression. Therefore, benzene should be used as a solvent carefully, avoiding evaporation in the open or inhaling its vapours.

Keeping in view the importance of aromatic compounds, we shall study some important electrophilic substitution reactions of benzene like nitration, halogenation and sulphonation in this unit. It is important to understand the pathway of any chemical reaction, so we will discuss the mechanism of these electrophilic substitution reactions. In addition to this, we will discuss Friedel-Crafts alkylation and Friedel-Crafts acylation of aromatic compounds. At the end we will learn some addition reactions, like chlorination and reduction of benzene. In the next unit, we will study reactions of alkylbenzene in detail.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ discuss the nitration, halogenations and sulphonation of benzene;
- ❖ discuss the Friedel-Crafts alkylation of benzene;
- ❖ explain the limitations of Friedel-Crafts alkylation reactions;
- ❖ discuss the Friedel-Crafts acylation of benzene;
- ❖ explain the mechanism of electrophilic substitution reactions of benzene;
- ❖ describe the addition reactions of benzene; and
- ❖ discuss reduction of benzene.

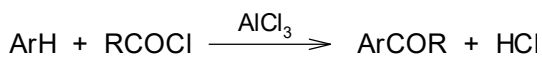
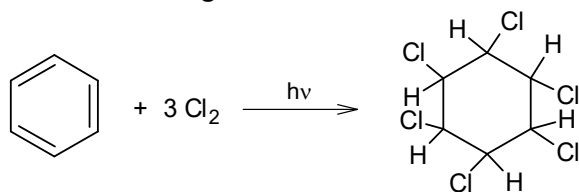
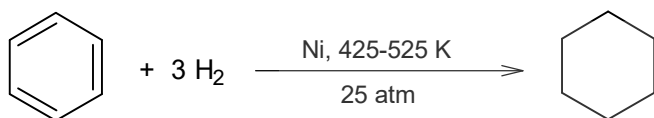
11.2 REACTIONS OF AROMATIC COMPOUNDS

The characteristic reactions of aromatic compounds are electrophilic substitution, in which the resonance-stabilised ring system is preserved. Why is this so? You may answer by saying that this is due to the resonance stabilisation of the benzene. But then the question arises, why then benzene enters into reactions at all, why is it not inert? This dual behaviour, the coexistence of stability and reactivity is due to the presence of the circulating π electrons in the benzene ring which, on one hand, keep the carbon nuclei within bonding distance and, on the other, offer a site of attack to positively charged species i.e. electrophile.

Electrophilic substitution includes a wide variety of reactions, such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation and Friedel-Crafts acylation reactions. Infact, electrophilic substitution reactions undergone by nearly all aromatic rings. In addition to electrophilic substitution reactions, benzene also undergoes few addition reactions. Some important reactions are summarised in Table 11.1.

Table 11.1: Reactions of Benzene

1) Nitration $\text{ArH} + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{ArNO}_2 + \text{H}_2\text{O}$
2) Halogenation $\text{ArH} + \text{X}_2 \xrightarrow{\text{Fe}} \text{ArX} + \text{HX}$
3) Sulphonation $\text{ArH} + \text{SO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{ArSO}_3\text{H} + \text{H}_2\text{O}$
4) Friedel-Crafts alkylation $\text{ArH} + \text{RCI} \xrightarrow{\text{AlCl}_3} \text{ArR} + \text{HCl}$

5) Friedel-Crafts acylation**6) Addition of halogen to benzene****7) Reduction of benzene**

Note: Ar = C₆H₅-

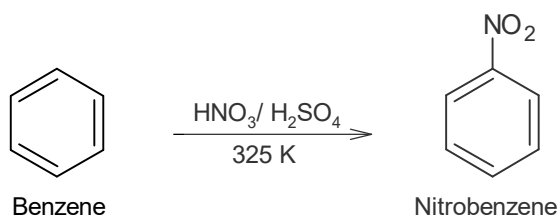
Let us study these reactions in detail.

11.3 ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

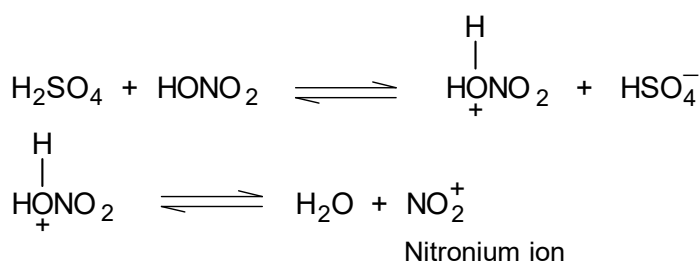
In this section, we will discuss some important electrophilic substitution reactions of aromatic compounds, taking example of benzene. The characteristic reactions of aromatic compounds are electrophilic substitution reactions. In these reactions electrophile attacks the aromatic π electrons and replaces one hydrogen atom of the aromatic ring. Benzene is a conjugated system with six π electrons, hence benzene acts as an electron donor in most of the reactions.

11.3.1 Nitration

Replacement of a hydrogen atom of the aromatic compound in the ring by the nitro-group is known as “**Nitration**”. The nitration of benzene gives nitrobenzene. Nitration of benzene can be carried out by reaction of benzene with a mixture of concentrated nitric and sulphuric acids.



The electrophile in this reaction is the nitronium ion, NO₂⁺. It is generated by the reaction of H₂SO₄ with HNO₃.



Further evidence for the participation of the nitronium ion comes from the fact that other species capable of producing nitronium ion, such as $\text{NO}_2^+ \text{BF}_4^-$, $\text{NO}_2^+ \text{NO}_3^-$ and $\text{NO}_2^+ \text{ClO}_4^-$ and also nitrate benzenoid compounds.

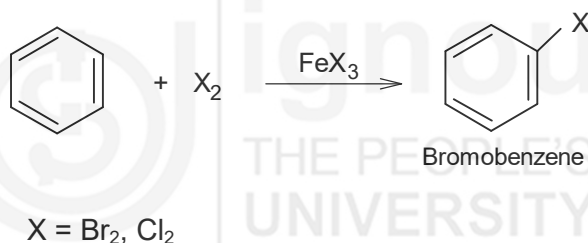
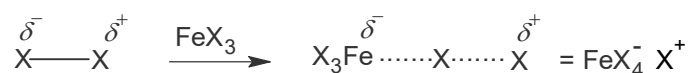
Nitration of benzene is an important reaction because the nitro group can be converted into other functional groups.

SAQ 1

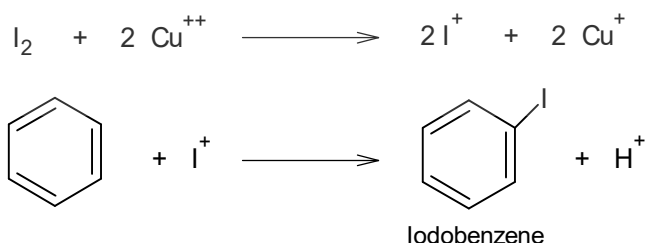
Give the reaction for generation of NO_2^+ .

11.3.2 Halogenation

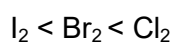
Normally benzene does not react with halogens. Halogens are not electrophilic enough to attack on aromatic ring. However, benzene reacts with halogens in the presence of Lewis acid as catalyst (FeBr_3 , FeCl_3) to yield halogen substituted products, i.e., aryl halides. In presence of a catalyst, halogens become a powerful electrophile. The main function of the catalyst is to partially or completely polarise the halogen-halogen bond and generate X^+ e.g.



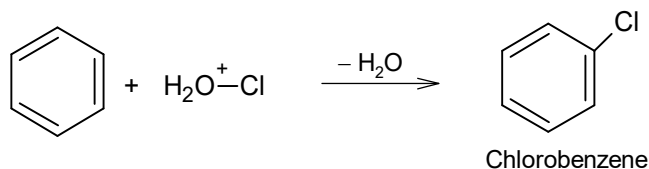
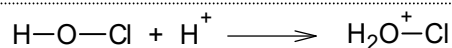
A typical reaction of aromatic halogenations is the bromination of benzene. As a general rule, fluorine is too reactive and a poor yield of fluorobenzene is obtained. Chlorine reacts smoothly and gives an excellent yield of chlorobenzene. Iodine itself is unreactive; however, iodination of benzene is carried out in the presence of oxidising agent such as hydrogen peroxide, H_2O_2 , or copper salt such as CuCl_2 . This oxidising agent oxidises molecular iodine to an electrophile I^+



Reactivity of halogens has the following order:



Halogenations can also be affected by other reagents, such as hypochlorous or hypobromous acids in presence of strong acids.



SAQ 2

Fill in the following blanks

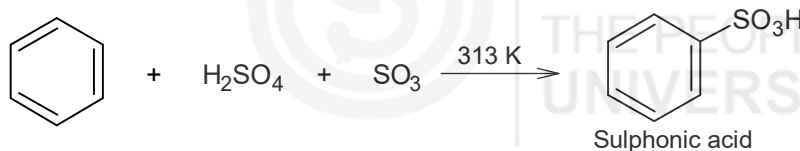
- Benzene reacts with halogen in presence of catalyst to produce
- The main function of catalyst is to polarise thebond.

11.3.3 Sulphonation

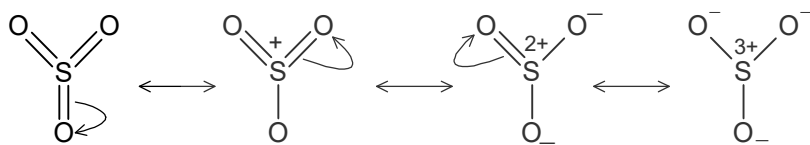
Benzene can be sulphonated by the reaction with fuming sulphuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$) Benzene reacts with HSO_3^+ to give benzenesulphonic acid.

Aromatic compounds in which the sulphonic group ($-\text{SO}_3\text{H}$) is directly attached to the benzene ring are called aromatic sulphonic acids.

Replacement of hydrogen of benzene by the sulphonic group is called sulphonation. This is another example of electrophilic substitution reaction. Sulphonation is usually accomplished using sulphuric acid or fuming sulphuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$) containing varying proportions of sulphur trioxide. This mixture is called "oleum".



Here the reactive species is neutral SO_3 , as is evident from its structure given below:



Unlike other electrophilic substitution reaction of benzene, sulphonation is a highly reversible reaction and the direction depends on the reaction conditions. Sulphonation is favoured in the presence of concentrated or fuming sulphuric acid, however, desulphonation is favoured in hot, dilute aqueous acids. Sulphonation is used in preparation of detergents and manufacture of dyes.

SAQ 3

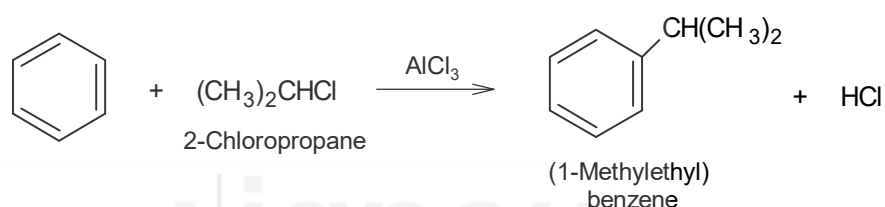
Fill in the following blanks:

- Sulphonation is an substitution reaction .
- Desulphonation is not possible in acid.

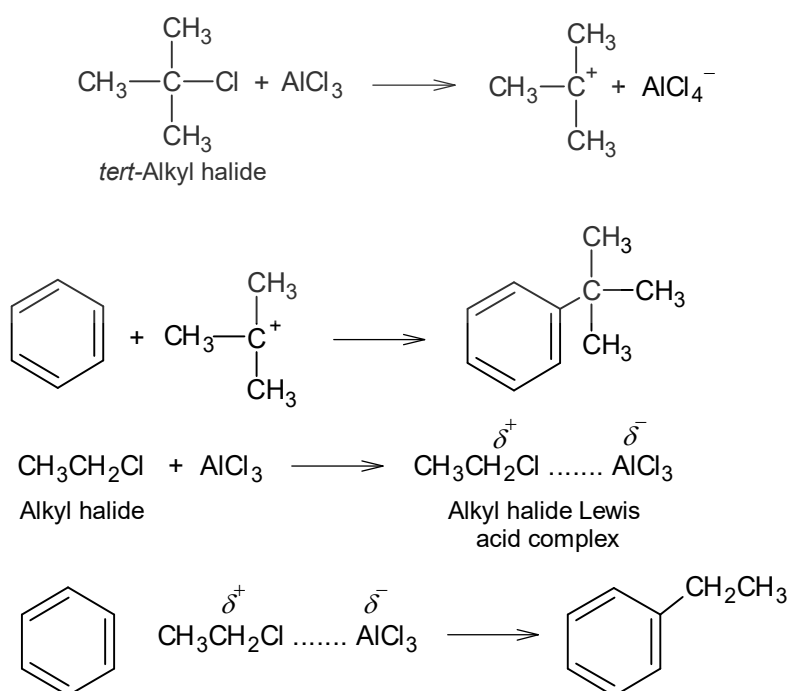
11.3.4 Friedel-Crafts Alkylation

In 1877 two scientists Freidel and Crafts discovered the alkylation of benzene in presence of AlCl_3 . Introduction of alkyl group in an aromatic ring is called Friedel-Craft alkylation. Complex substituted aromatic compounds are almost always synthesised from the simpler, readily available aromatic compounds. Since benzene is very common and easily available, chemists use it as starting material and introduce the desired substituents. You have already studied the introduction of halogen, nitrogen and sulphur-based functional groups in the aromatic ring. Now you will study another important reaction, i.e., alkylation of aromatic ring.

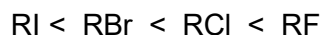
Reaction of benzene with haloalkane in presence of aluminium halide gives alkylbenzene and hydrogen halide. This reaction is known as Friedel-Craft alkylation. Friedel-Craft alkylation can also take place in presence of any other Lewis acid as catalyst. The reaction of 2-chloropropane with benzene in the presence of AlCl_3 to yield (1-methylethyl) benzene is a typical Friedel-Crafts alkylation reaction.



The electrophile in the Friedel-Crafts reaction is R^+ . This ion is formed when an alkyl halide reacts with a Lewis acid. Lewis acids, such as AlCl_3 , FeCl_3 , ZnCl_2 , AlBr_3 , BF_3 etc. are used in Friedel-Crafts alkylations. In case of alkylation with tertiary alkyl halides, the electrophilic species is a free carbocation. However, in primary and secondary alkyl halides, it appears that instead of free carbocations, the electrophilic species is an alkyl halide Lewis acid complex with positively polarised carbon.



The reactivity of haloalkane increases with polarity of C—X bond. The order is:

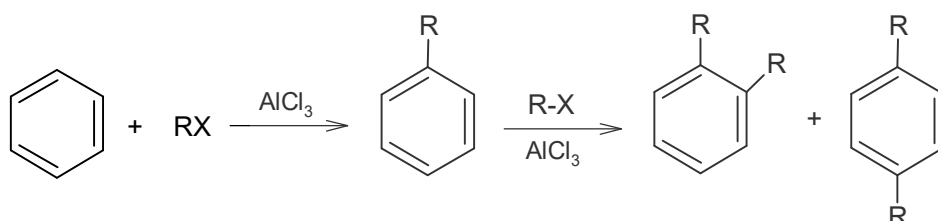


R= Alkyl group

Friedel-Crafts reaction is widely applicable in organic synthesis. However, it has some limitations, which are given below:

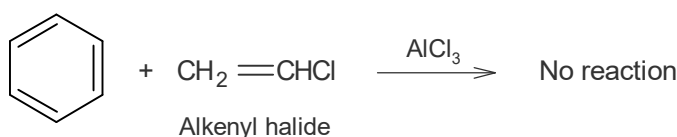
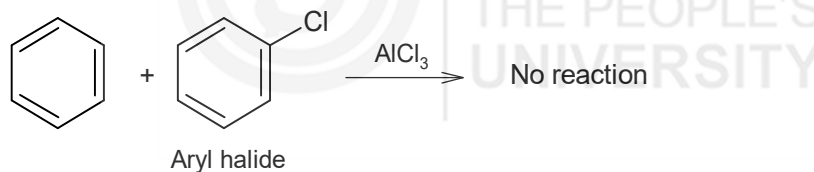
Limitations of Friedel-Crafts Alkylation

- i) The main difficulty with the Friedel-Crafts alkylation is that the substitution of the first alkyl group activates the ring towards further substitution.

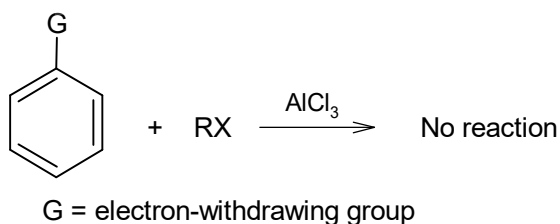


The best way of avoiding this second reaction is to use an excess of aromatic compound.

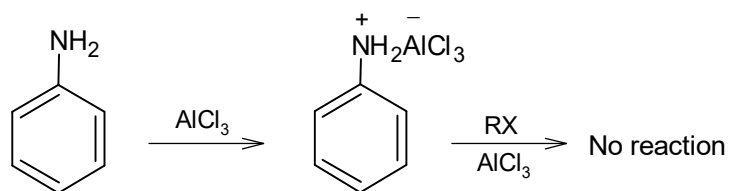
- ii) Friedel-Crafts alkylation reactions are limited to alkyl halides, aryl halides and alkenyl halides do not react. This is because aryl and alkenyl carbocations are too unstable to form under Friedel-Crafts reaction conditions.



- iii) If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation since the deactivated ring is not reactive to attack by carbocations.

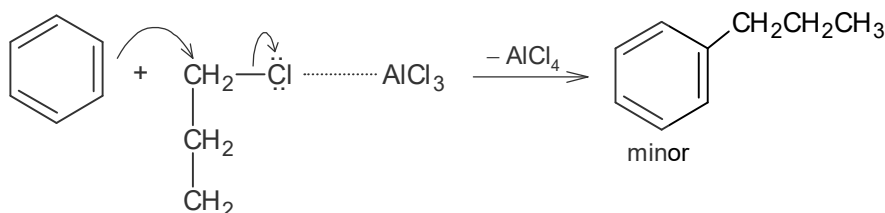


- iv) Aromatic amines fail to undergo alkylation, probably because amino group forms a complex with Lewis acid. Since this complex has a positive charge on nitrogen, it deactivates the aromatic ring for electrophilic substitution.

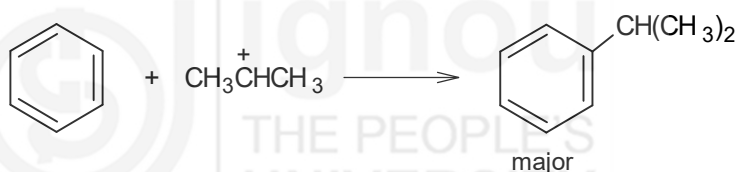
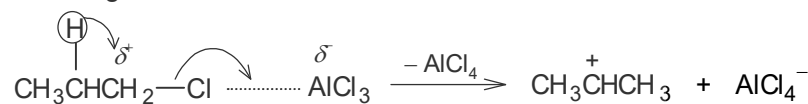


- v) Sometimes during the alkylation, the attacking electrophile undergoes rearrangement by 1, 2-shift of H or R. For example, the alkylation of benzene with 1-chloropropane leads to a mixture of *n*-propylbenzene and (1-methyl)ethyl benzene.

No rearrangement



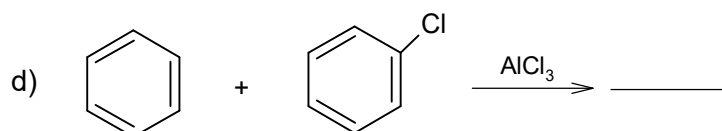
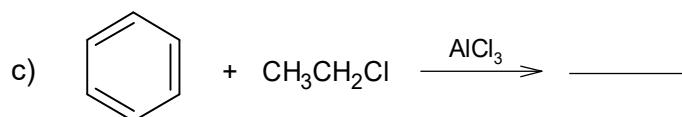
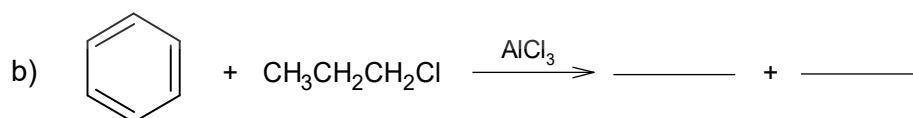
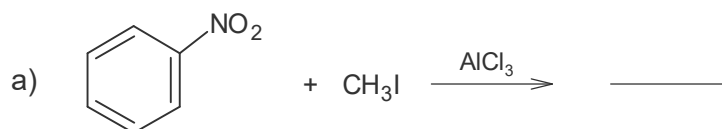
Rearrangement



The mechanism is similar to alkylation with an alkyl halide and this reaction proceeds through the more stable carbocation intermediate.

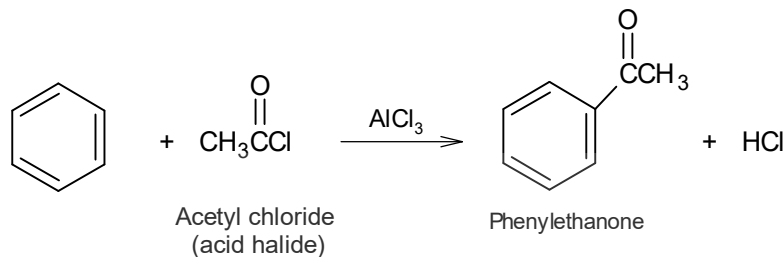
SAQ 4

Give the product(s) of the following reactions:



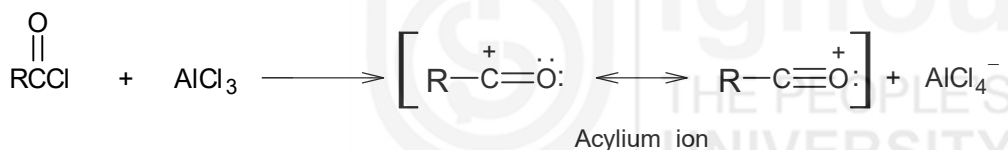
11.3.5 Friedel-Crafts Acylation

The RCO— group or ArCO— group is called an acyl group. Substitution of an acyl group into an aromatic ring by the reaction with an acid chloride in the presence of Lewis acid as catalyst is called Friedel-Crafts acylation. For example, the reaction of benzene with ethanoyl chloride (acetyl chloride) gives the ketone, phenylethanone (acetophenone).

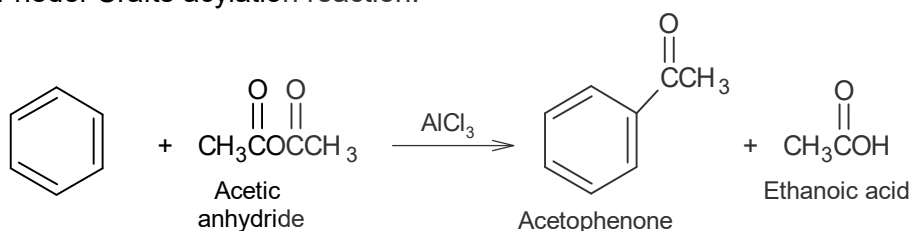


The Friedel-Craft acylation is very important reaction in organic chemistry. It has many applications e.g. It is an excellent method for synthesis of aromatic ketones.

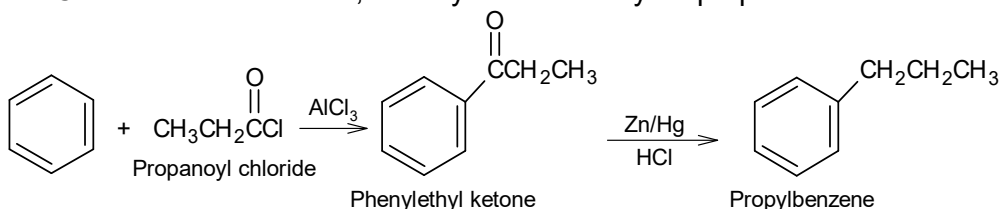
The mechanism of Friedel-Crafts acylation, which we will explain in section 11.3.6, is similar to other electrophilic aromatic substitution reactions. The electrophile in this reaction is the resonance stabilised carbocation, **acylium ion**. This ion is formed when the acid chloride reacts with the Lewis acid, AlCl_3 .



Carboxylic acid anhydrides can be used as alternative to acid chlorides for the Friedel-Crafts acylation reaction.



Friedel-Crafts acylation reaction is synthetically useful reaction. For example the carbonyl group of the ketone produced by Friedel-Crafts acylation can be reduced to $>\text{CH}_2$ group by using zinc amalgam and hydrochloric acid. This method of reduction is known as Clemmensen reduction which you have studied in Unit-10 of this course. By the combination of Friedel-Crafts acylation and Clemmensen reduction, an alkylbenzene may be prepared.



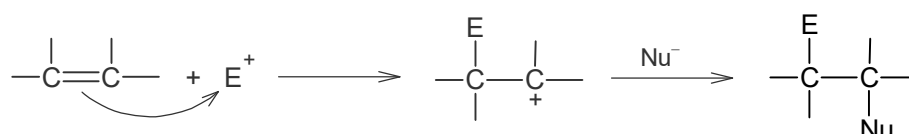
Unlike Friedel-Crafts alkylation, Friedel-Crafts acylation reactions are not accompanied by rearrangements within the acyl group. Moreover, there is no

polysubstitution as the aromatic ring is deactivated after the introduction of the first acyl group. Acylation reactions are free from limitations of alkylation reactions. Secondly, acylium ions do not undergo rearrangements.

11.3.6 Mechanism of Electrophilic Substitution

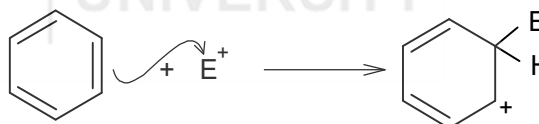
All the electrophilic substitution reactions take place by similar mechanism. It is necessary to understand the principles of this mechanism. Thus, we will discuss the general electrophilic substitution mechanism by using E^+ for electrophiles.

Before studying detailed mechanism, let us briefly recall what we have learnt about electrophilic addition to alkenes. Electrophilic attack on $C=C$ gives carbocation intermediate which is then attacked by nucleophile to yield addition product.

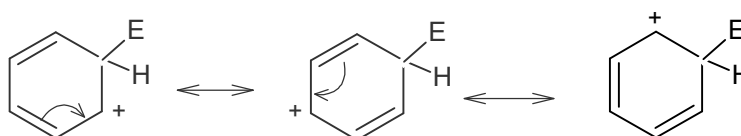


An electrophilic aromatic substitution reaction begins in a similar way. The π electrons of the ring attack on electrophile E^+ , forming a σ bond with electrophile. In this process, the positive charge of the electrophile is transferred to the adjacent ring carbon atom which is called carbonation. This is a slow step and is, therefore, the rate determining step.

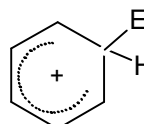
Formation of $C-E$ bond converts sp^2 hybridised carbon to sp^3 hybridised carbon atom of the ring, which disturb the conjugation of benzene ring. Hence, the resulting intermediate is not aromatic.



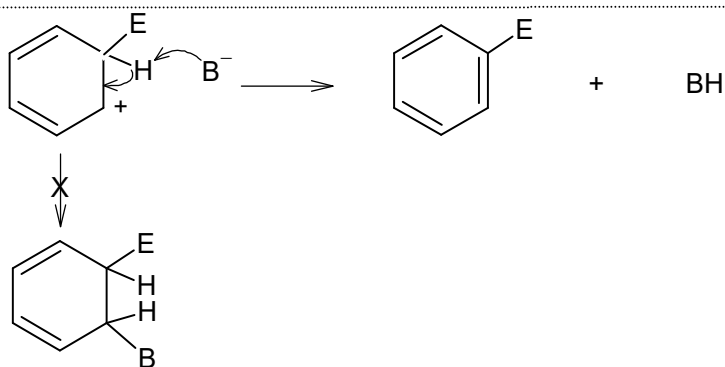
This carbocation is stabilised by resonance as shown below:



These three resonance structures of the intermediate are often combined and represented as follows:



In the case of alkenes, you have seen that nucleophile attacks the carbocation to yield the addition product. Since, in the present case, the addition of the nucleophile would destroy the aromatic stabilisation of the benzene ring, this type of addition does not take place in aromatic carbocations. Instead, nucleophile acts as base and abstracts a ring proton yielding substituted aromatic product.



This reaction is exothermic in nature because C—E bond is stronger than C—H bond. The potential energy diagram (Fig.11.1) of electrophilic substitution reaction of benzene also confirmed that this is an exothermic reaction.

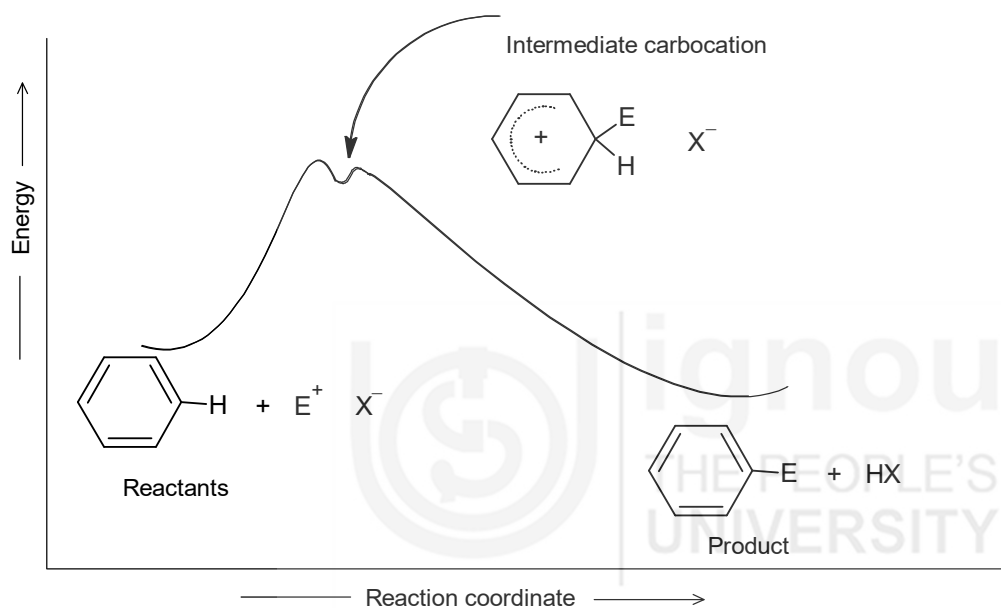
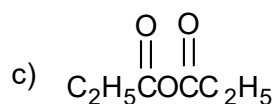
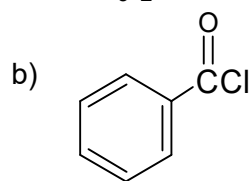
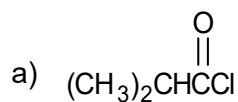


Fig. 11.1: Potential energy diagram for an electrophilic substitution reaction of benzene.

SAQ 5

Give the structure of the product expected from the reaction of each of the following compounds with benzene in the presence of AlCl_3 .

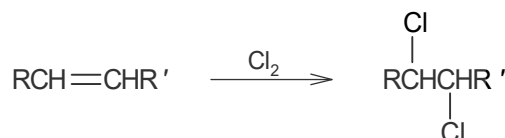


11.4 ADDITION REACTIONS OF BENZENE

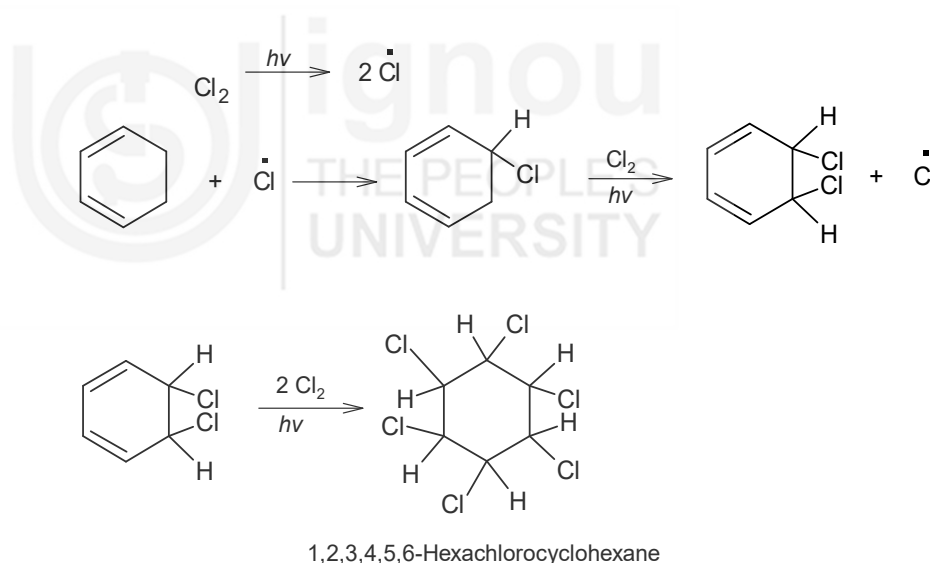
In addition to electrophilic substitution reactions, benzene also undergoes few addition reactions, e.g. addition of halogens to benzene and addition of hydrogen to benzene (reduction of benzene). Let us discuss these reactions in little detail.

11.4.1 Addition of Halogen to Benzene

You have already studied in the first semester that addition of chlorine to an alkene gives 1,2-dichloroalkane.



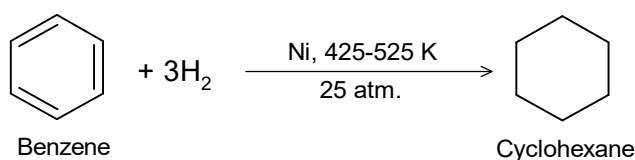
In contrast to this, the addition of chlorine to benzene takes place with some difficulty and produces several isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes. In the presence of sunlight, benzene gives an addition product. For example, when treated with chlorine or bromine in the presence of sunlight, benzene forms the benzenehexachloride ($\text{C}_6\text{H}_6\text{Cl}_6$, known as gammaxene) and benzenehexabromide ($\text{C}_6\text{H}_6\text{Br}_6$) respectively. These addition reactions proceed by the free radical mechanism.



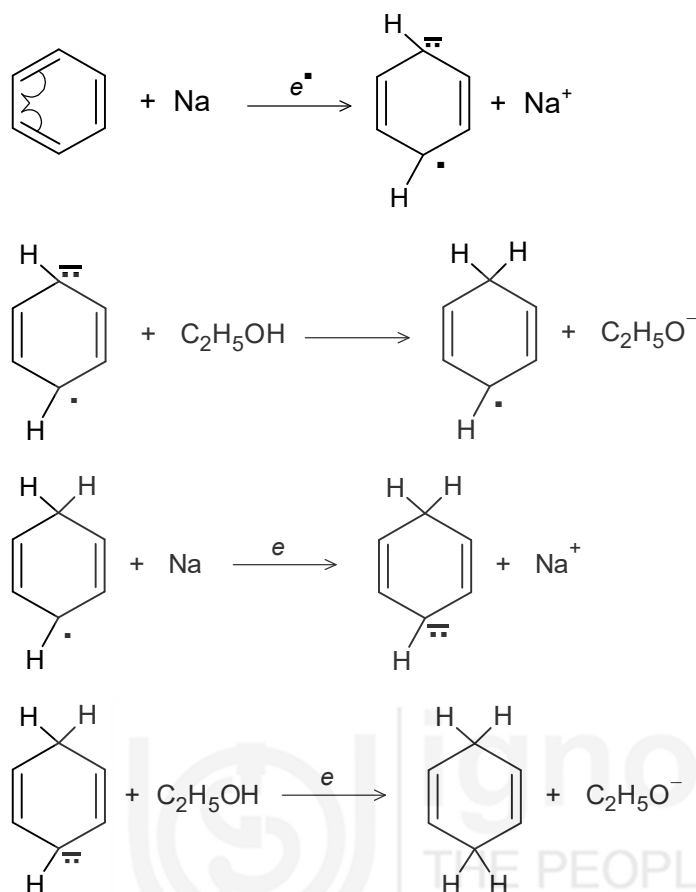
The 1,2,3,4,5,6-hexachlorocyclohexane, theoretically can exist in eight stereoisomerism forms but only seven of these are known. One of the isomers, is gammaxene, is a powerful insecticide. It is very stable and acts more quickly than DDT. Remember all the isomers exist in chair form.

11.4.2 Reduction of benzene

Hydrogenation of benzene at higher temperature and under pressure yields cyclohexane.



Although benzene is not reduced by metals and acid, or by sodium in ethanol, it is reduced by sodium in liquid ammonia in the presence of ethanol (Birch reduction) to give 1, 4-dihydrobenzene (cyclohexa-1, 4-diene). This reaction has also been shown to have free radical mechanism.



Lithium in anhydrous ethylamine, however, reduces benzene to cyclohexene and cyclohexane.

SAQ 6

Give the mechanism of conversion of benzene to cyclohexane.

11.5 SUMMARY

In this unit you have studied that:

- Unlike alkenes, benzene does not undergo addition reactions but it undergoes electrophilic substitution reactions, e.g., nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation etc.
- Nitration of benzene gives nitrobenzene. Nitration of benzene can be carried out by reaction of benzene with a mixture of concentrated nitric and sulphuric acids.
- Benzene reacts with halogens in the presence of a catalyst (AlCl_3 , FeBr_3 , FeCl_3) to give aryl halides. Fluorine is too reactive and a poor yield of

fluorobenzene is obtained. Chlorine reacts smoothly and gives an excellent yield of chlorobenzene. Iodine is unreactive; however, iodination of benzene is carried out in the presence of oxidising agent such as hydrogen peroxide.

- Benzene reacts with SO_3 to give benzenesulphonic acid. Sulphonation is usually accomplished using sulphuric acid or fuming sulphuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$) containing varying proportions of sulphur trioxide. Sulphonation is a highly reversible reaction.
- Reaction of aromatic compounds with alkyl halides in presence of anhydrous AlCl_3 as catalyst gives alkylated products. This reaction is known as Friedel-Crafts alkylation. This Friedel-Crafts reaction is widely applicable in organic synthesis, but it has some limitations e.g. The first alkyl group activates the ring towards further substitution. Friedel-Crafts alkylation reactions are limited to alkyl halides; aryl halides and alkenyl halides do not react. Sometimes during the alkylation, the attacking electrophile undergoes rearrangement by 1, 2-shift of H or R. Aromatic amines fail to undergo alkylation. If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation.
- Substitution of an acyl group into an aromatic ring by reaction with acid chlorides in presence of Lewis acid as catalyst is called an aromatic acylation reaction or Friedel-Crafts acylation.
- The addition of chlorine to benzene takes place with some difficulty. In the presence of sunlight, benzene gives an addition product. Several isomers are 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes are obtained.

11.6 TERMINAL QUESTIONS

1. Arrange the following compounds in the expected order of the reactivity towards Friedel-Crafts alkylation.



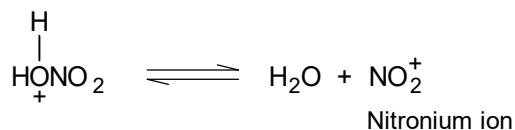
2. How do you convert benzene to the following compounds?
 - a) Bromobenzene
 - b) Benzenesulphonic acid
 - c) Cyclohexane
 - d) Ethylbenzene
 - e) Hexachlorocyclohexane
3. Write the mechanism of sulphonation of benzene using SO_3 as electrophile.

11.7 ANSWERS

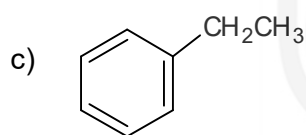
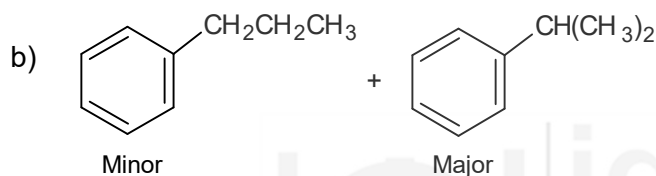
Self-Assessment Questions

1. The electrophile in this reaction is the nitronium ion, NO_2^+ . It is

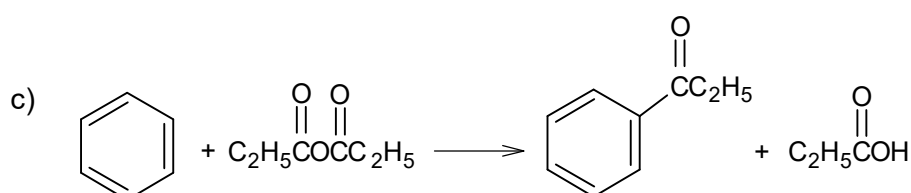
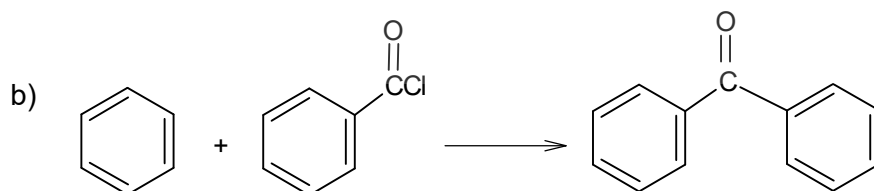
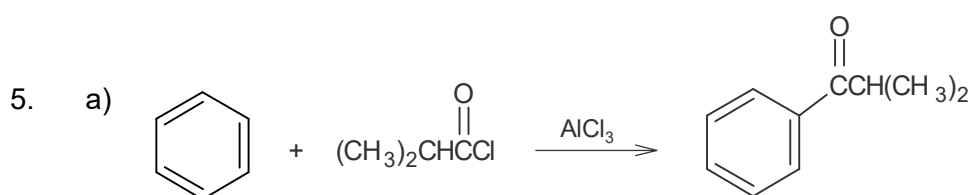
generated by the reaction of H_2SO_4 with HNO_3 .

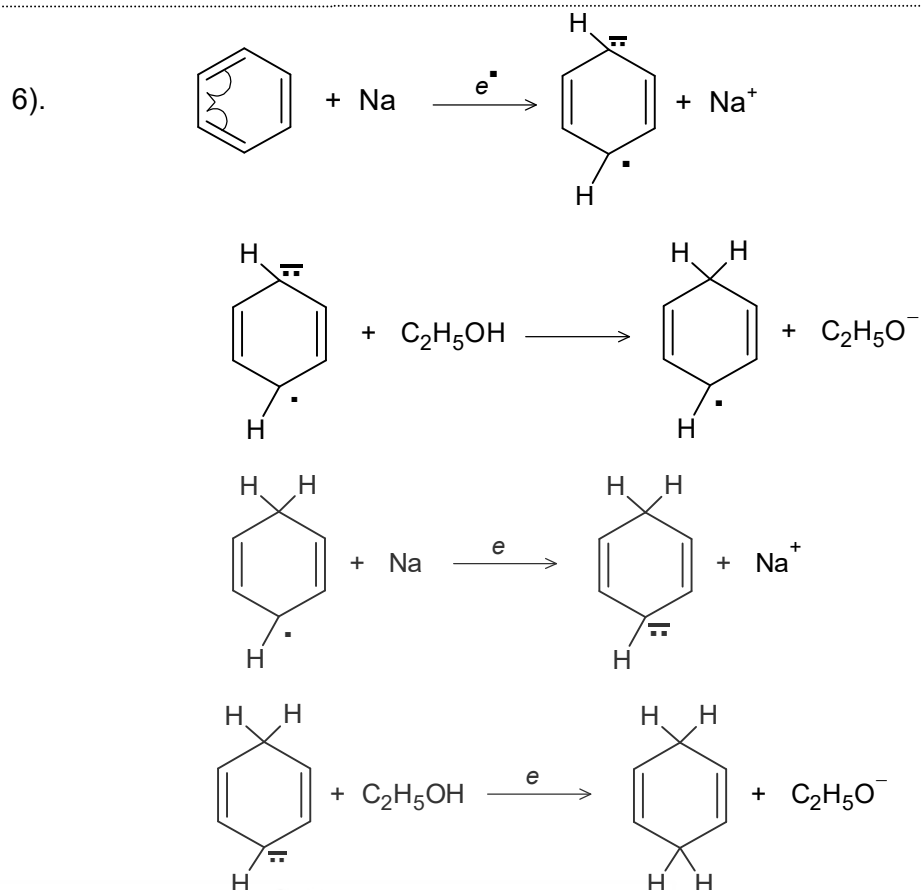


2. i) aryl halide
- ii) halogen-halogen
3. i) Electrophilic
- ii) hot aqueous
4. a) No reaction.



- d) No reaction.





Similarly, following same step we get cyclohexane.

Terminal Questions

1. Reactivity increases as follows:

